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16. ABSTRACT

The accurate measurement of annual average mineral fiber concentrations at various air sampling sites provides the best index of non-occupational inhalation exposure to fibers in a community located near an industrial source of airborne amphibole fibers. The transmission electron microscope analysis of enough individual high volume air samples to provide annual average fiber concentrations is not feasible because of the great time and expense required. X-ray diffraction analysis of air samples collected on membrane filters over periods of several days offers a reliable measurement of amphibole mineral mass concentration. An excellent linear correlation ($r = 0.94$ for $N = 12$) exists between the amphibole mass concentrations (x-ray diffraction) and amphibole fiber concentrations (transmission electron microscope). The correlation equation is used to calculate amphibole fiber concentrations from over 300 x-ray diffraction analyses. The accuracy and precision of both techniques are discussed as well as particle concentration variations influenced by meteorology, emission sources, and sampling location.

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CHAPTER 11

AMPHIBOLE FIBER CONCENTRATION DETERMINATION FOR A SERIES OF COMMUNITY AIR SAMPLES: USE OF X-RAY DIFFRACTION TO SUPPLEMENT ELECTRON MICROSCOPE ANALYSIS

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INTRODUCTION

Environmental health studies require accurate and detailed measurements of the toxicant concentrations to which populations are exposed over time. Concentrations of airborne particles such as mineral fibers can vary greatly depending on distance from sources, meteorological conditions and variations in emission rates. Occasional peak concentrations may constitute a major portion of the total exposure. The ideal analytical scheme for measuring the exposure history of a population should accurately determine the accumulated dose and also measure fluctuations in exposure.

The processing of taconite rock (iron ore) in Silver Bay, Minnesota, results in the loss into the air of amphibole fibers from the crushed rocks through stack emissions and fugitive dust. The residential area of Silver Bay is approximately one kilometer northwest of the general area of dust emissions.

Most of the amphibole fibers found in air samples from the area are cummingtonite-grunerite or actinolite. Extensive air monitoring has been conducted in recent years because of the similarity of many of these fibers to amosite fibers which are known to cause lung cancer, mesothelioma and asbestosis in humans following inhalation exposure (Selikoff *et al.*, 1972). The amphibole fibers range from blocky particles of 3:1 length-to-diameter ratio to thin fibers, or bundles of thin fibers, with length-to-diameter ratios occasionally larger than 20:1. Larger diameter inorganic particles in the air include quartz, hematite, fly ash, magnetite, pyroxene, gypsum and nonfibrous amphibole.

The Minneosta Department of Health has maintained a high-volume air sampler at each of the three schools in Silver Bay (Figure 1) since December 1973. These samplers collect airborne particulate on 1.2-μm membrane filters. The normal sample collection period is one week, with a cycle of three hours off and one hour on, maintained with flow rates of about 0.6 m^3/min through an effective filtration area of 406 cm^2. The membrane filters

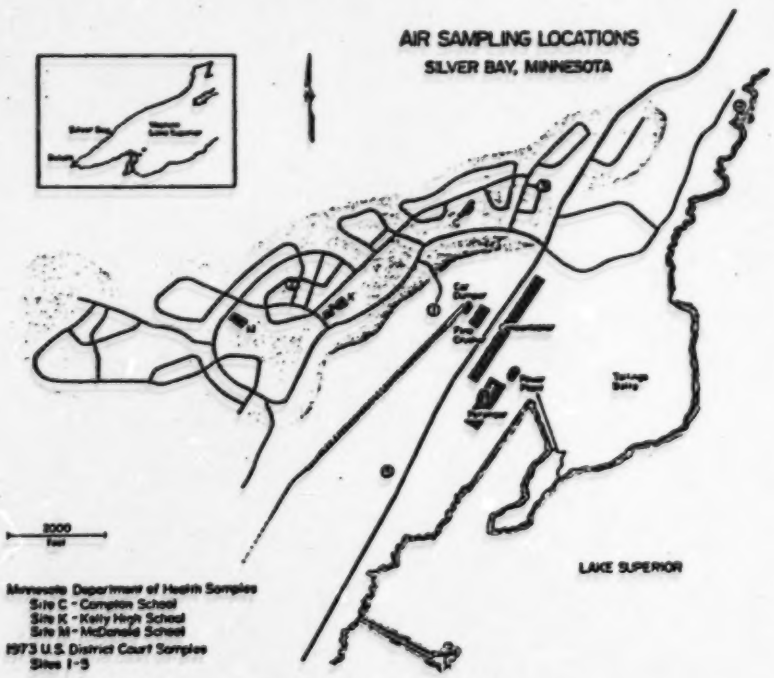
AIR SAMPLING LOCATIONS
SILVER BAY, MINNESOTA
LAKE SUPERIOR
Minnesota Department of Health Samples
Site C - Compton School
Site K - Kelly High School
Site M - McDonald School
1973 U.S. District Court Samples
Sites 1-3

Figure 1. Air sampling locations.

thus contain a loading of particles that is too heavy for direct transfer to electron microscope grids for fiber counting but is suitable for direct X-ray diffraction analysis of amphibole mineral concentration.

X-Ray diffraction was used to rapidly and inexpensively determine amphibole mass concentrations for over 500 air samples from Silver Bay. The analysis was found to be a useful indicator of periodic fluctuations in amphibole particle concentrations and made possible the determination of mean annual amphibole fiber concentrations at the three school sampling sites.

EXPERIMENTAL

Electron Microscope Analysis

Selected air samples were analyzed with a JEOL[1] 100C transmission electron microscope for amphibole fiber concentration. Twelve membrane filter samples were initially chosen to represent each of the three school locations for each season of 1975. The heavy particle loading on the filters required a sample dilution step prior to electron microscope grid preparation. Detailed procedures which will be described elsewhere (Cook *et al.*, in preparation) involved low-temperature ashing of a piece of the original membrane filter, resuspension of the ash in filtered distilled water with 5 min of low-energy sonification, and filtration on a 47-mm 0.1- or 0.2-μm Nuclepore filter. After the Nuclepore filter is carbon-coated, small pieces are placed on electron microscope grids and the filter material dissolved by chloroform with a modified Jaffe wash procedure previously described for the preparation of water samples (Cook *et al.*, 1976). The carbon film containing the air sample particles is left on the grid.

Electron microscope examination of the grids was performed by systematically scanning grid openings at 10,000X magnification. Each particle with a length-to-width ratio greater than or equal to 3:1 was studied by selected-area electron diffraction. Amphibole fibers were positively identified by observation of characteristic layer lines with a 5.3 Å reciprocal repeat and an arrangement of diffraction spots like those in diffraction patterns produced by standard samples of amphibole minerals. (100) and (110) sections were most commonly observed. Energy-dispersive X-ray spectra were obtained for some fibers in order to determine elemental composition.

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[1]The name of a specific manufacturer's product is used for identification purposes only and does not constitute endorsement by the U.S. Environmental Protection Agency.

X-Ray Diffraction Analysis

Samples were prepared for X-ray diffraction analysis by simply mounting the membrane filter on a 17-mm x 26-mm piece of glass cut from a microscope slide. A light coating of clear lacquer sprayed on the glass provided a smooth effective adhesive for the filter piece which was then trimmed with a razor blade to the edge of the glass. For air samples, a light coating of lacquer was sprayed on the filter-sample surface prior to mounting on the glass piece as some dust particles could rub off without this protection. The layer of lacquer causes a small loss of X-ray intensity due to scattering of X-rays.

The glass slide with attached filter piece was mounted in an aluminum sample holder which was inserted in a cassette used for the automatic sample changer on a Phillips APD 3500 powder diffractometer. The filter sample was held flush with the top surface of the aluminum sample holder by sealing the reverse side of the sample into the holder with a few drops of hot wax. The automatic sample changer accommodates up to 35 samples and standards so sample preparation and data collection involve very little time.

Amphibole mineral quantitative analysis was based on measurement of the amphibole (110) peak intensity as previously described (Cook, 1975). No peak interferences from other minerals were found in background air samples over the 2θ range of 9.9 to 11.1 degrees scanned with copper-Kα radiation. The X-ray source was a long-anode fine-focus copper tube operated at 45 kV and 40 mA. Diffraction peak X-ray intensity was maximized by using a 9° take-off angle. The vertical diffractometer was equipped with a graphite crystal focusing monochromator and scintillation detector. Each sample was step-scanned in 0.02° 2θ increments at a rate of 0.25° 2θ per minute. Integrated peak intensity determined by computer subtraction of background X-ray intensity for each 2θ increment was recorded on a teletypewriter.

An external standard technique was used to calculate amphibole mass concentrations. Similar techniques have been used to estimate chrysotile and amphibole concentrations in dust samples on membrane filters (Rickards, 1972; Crable, 1966). The external standard chosen for preparation of a standard curve (Figure 2) was the same amphibole mixture found in $< 2\ \mu m$ taconite tailings used in Lake Superior water sample analysis (Cook, 1975). The fine tailings contain approximately 80% amphibole, mostly cummingtonite-grunerite with some actinolite. The remaining 20% is quartz with traces of other minerals. The amphibole fibers in the standard are essentially the same as those present in air samples from Silver Bay but tend to have a smaller diameter distribution. Standard samples were prepared by filtration of known amounts of amphibole mixture on 960 mm^2 areas of Millipore filters.

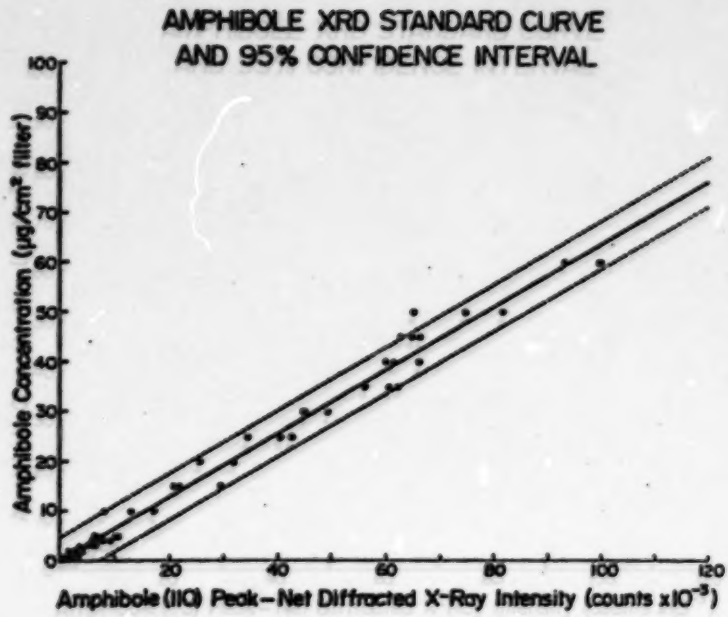

Figure 2. External standard curve for amphibole mass concentration analysis.

Each filter was coated with lacquer and mounted for X-ray diffraction analysis in the same way as the air sample filters. A linear relationship was found to exist for X-ray intensity versus mass of amphibole over the range of amphibole masses found in Silver Bay air samples (Figure 2). The 95% confidence interval for a single sample measurement is shown in Figure 2. The variability of the diffractometer measurement and of the preparation of known trace amounts of amphibole on filters mounted for X-ray diffraction analysis both contribute to the size of this 95% confidence interval.

UTILITY OF THE X-RAY DIFFRACTION TECHNIQUE

Accuracy and Precision

The X-ray diffraction analysis of thin layers of dust on membrane filters can have error introduced by such factors as variable degrees of preferred orientation, absorption of X-rays and differences in particle size distributions.

The preferred orientation of amphibole fibers and cleavage fragments, laying on their c-axis as collected on a membrane filter, is desired in order to

achieve maximum (110) X-ray diffraction peak intensity. The linear relationship between amount of amphibole and diffracted X-ray intensity (Figure 2) indicates no loss of preferred orientation over the range of amphibole concentrations found in the air samples studies. Loss of preferred orientation in air samples due to a heavy loading of other particles would result in a decrease in amphibole (110) peak intensity and an underestimate of amphibole concentration.

Samples mounted on membrane filters for X-ray diffraction analysis with less than "infinite thickness" are subject to variable sample matrix absorption of X-rays unless the samples are thin enough to cause very little absorption. The linearity of the relationship between X-ray intensity and amphibole mass for standard samples indicates that for amphibole mass loading up to 0.2 mg/cm^2 of filter, no appreciable X-ray absorption occurs. A slight nonlinearity of this relationship for mass loadings of 0.2 to 0.5 mg/cm^2 is probably caused primarily by decreasing degree of preferred orientation rather than an absorption effect. Evidence for this conclusion is found in the uniform intensity of filter background X-ray intensity over this range of sample loading.

Actual air-sample total-mass loadings were calculated indirectly from total suspended-particulate concentrations determined for the same sampling periods. Heavy sample loadings were about 0.5 mg/cm^2 of filter while average sample loadings were about 0.2 mg/cm^2 of filter. The presence of many iron oxide particles in the air samples could contribute to an absorption loss of X-ray intensity, especially for those samples with heavy filter loading, and thus an underestimate of amphibole concentration.

Variation in amphibole particle size distribution from sample to sample would contribute to scatter in calculated amphibole concentrations based on the standard curve employing a < 2-μm gravity-sized amphibole mixture. Some amphibole particles in the air samples observed by electron microscope are too large to be found in a < 2-μm size distribution. The presence of these large particles should contribute to some systematic overestimate of amphibole concentrations.

Replicate analyses with different pieces of the same filter were performed for several samples. Standard deviations for groups of five replicates from those air samples with average amphibole concentrations were approximately 20% of the mean amphibole mass concentrations. Replicate analysis of samples with concentrations of amphibole close to the detection limit of 2.0 $\mu g/cm^2$ of filter (approximately 0.5 $\mu g/m^3$ of air in typical samples studied) yield standard deviations which equal a larger percent of the mean concentration. Replicate diffractometer analyses of the same sample preparations indicate that 50% or more of the imprecision found in the analysis of average samples is related to diffraction peak-intensity measurement.

Refinement of the sample preparation method and X-ray diffraction peak measurement would undoubtedly improve precision, accuracy and the detection limit. A very sensitive X-ray diffraction technique for the quantitative analysis of chrysotile has been reported (Birks *et al.*, 1975), for example. The primary purpose of this study, however, was to rapidly measure, directly from the membrane filters, the amphibole mass concentration with enough precision to allow an estimate of amphibole fiber concentrations.

Agreement Between X-Ray Diffraction and Electron Microscope Measurements

The ultimate use of the X-ray diffraction analysis of Silver Bay air samples is as a measure of amphibole fiber concentrations. The transmission electron microscope analysis of several hundred air samples is not feasible due to the time and cost involved. A strong correlation ($r = 0.94$) was found between the amphibole fiber concentrations measured by electron microscopy for the 12 selected Minnesota Department of Health air samples and the amphibole mass concentrations determined by X-ray diffraction for the same samples (Figure 3). The correlation is significant at the 99% confidence level and the

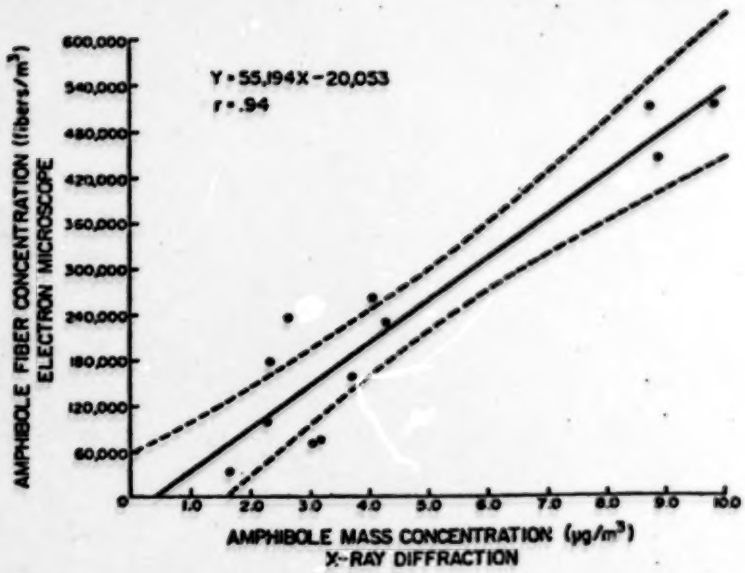

Figure 3. Regression line and 95% confidence interval for the association of amphibole mass concentration and amphibole fiber concentration for 12 representative air samples.

twelve samples cover the range of amphibole concentrations measured for almost all air samples. Thus an average annual amphibole fiber concentration can be calculated for each sampling site from the X-ray diffraction data which represents air sampling of every third hour throughout the year. Since an average annual amphibole mass calculation is based on 54 individual X-ray diffraction measurements, the 95% confidence interval for the determination of an average annual amphibole fiber concentration is actually narrower than that shown in Figure 3 (dashed lines).

The mean fiber concentration for the 12 air samples studied by transmission electron microscopy was 2.3×10^5 positively identified amphibole fibers per cubic meter of air. The mean amphibole fiber mass for all 12 samples was calculated to be 1.42 $\mu g/m^3$ based on an amphibole specific gravity of 3.4 g/cm^3 and fiber thickness equal to the fiber width measured on the electron microscope (overestimate likely). The mean total amphibole mass concentration determined for the 12 samples by X-ray diffraction was 4.56 $\mu g/m^3$. The difference between the amphibole fiber mass and total amphibole particle mass concentrations can be explained in part by the problem of positively identifying all amphibole fibers by electron microscopy: often the fibers are too small but occasionally they are too thick for electron diffraction. A more important factor is probably the presence of large amphibole particles that do not have 3:1 length-to-width ratios and represent a substantial percent of the total amphibole particle mass.

MONITORING DATA RESULTS AND DISCUSSION

The amphibole mass concentrations from the X-ray diffraction analysis of weekly Silver Bay air samples from these locations during 1974 and 1975 are plotted in Figure 4. Concentrations ranged from below the detection limit (generally about 0.5 $\mu g/m^3$) to a high of 15.8 $\mu g/m^3$.

High concentrations were found at all three sampling sites during the spring and early summer months, while lower concentrations were found during the fall and winter months. This tendency, which was observed each year, can be attributed to meteorological conditions. Low concentrations are associated with west-to-north winds and high concentrations are found during periods of south-to-east winds or no wind. The most significant meteorological event associated with high concentrations appears to be temperature inversion with air stagnation. This occurs along the shore of Lake Superior during spring and early summer when cold air from the lake moves onshore to become trapped under a warm-air layer aloft. This condition favors transport of dust emitted from the taconite processing facility (Figure 1) into residential Silver Bay where amphibole fiber concentrations rise due to the absence of winds to remove the airborne dust.

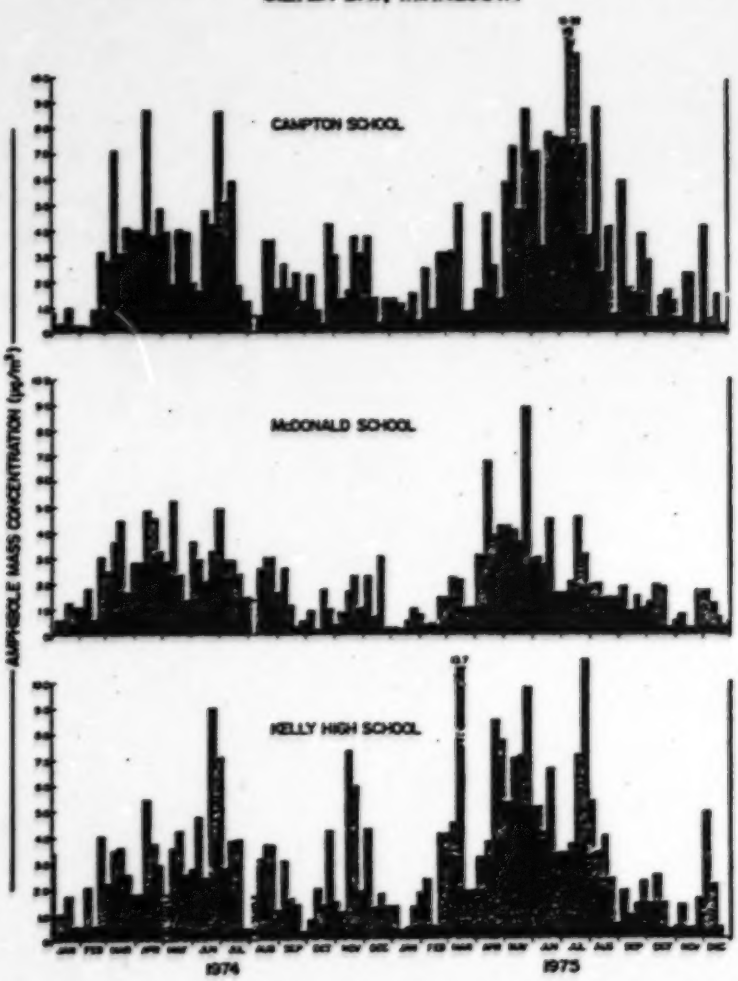

Figure 4. X-Ray diffraction analysis results for Silver Bay air samples.

Annual average amphibole fiber concentrations computed from the X-ray diffraction data shown in Figure 4 are listed in Table I. The McDonald School sampling site has the lowest concentration for each year studied as is expected by its location furthest from the dust sources. A comparison of McDonald School data with Kelly High School data indicates that peak

concentrations tend to occur simultaneously at these two sites. This phenomenon is consistent with the location of both sites west of the taconite processing facilities.

Table I. Mean Annual Air Concentrations—Silver Bay, Minnesota

Location	Amphibole Mass for the year ($\mu g/m^3$)			Amphibole Fibers for the year (fibers/m^3)		
	1974	1975	1976	1974	1975	1976
Kelly High School	2.74	3.54	2.42	1.31×10^5	1.75×10^5	1.14×10^5
Campton School	2.75	3.59	2.59	1.32×10^5	1.78×10^5	1.23×10^5
McDonald School	2.10	2.00	2.07	0.96×10^5	0.90×10^5	0.94×10^5

A second set of air samples were collected during the summer of 1976 at the three sampling sites by the University of Minnesota-Duluth for the Environmental Protection Agency. Air was sampled continuously with low-volume samplers for two days rather than the weekly intermittent sampling conducted by the Minnesota Department of Health. Sample loading was similar for both sets of samples. A comparison was made (Figure 5) of these two independent sets of samples by averaging the two-day samples to obtain concentrations that represent the same seven-day sampling periods used by the Minnesota Department of Health.

There is reasonably good agreement between these two sets of data, especially considering the different sampling techniques used and the difference in total hours sampled. All errors associated with sample collection, handling, preparation and X-ray diffraction analysis contribute to differences in the two sets of data. Linear regression analysis indicates highly significant correlations for each site between the two sets of ten data points: $r = 0.89$ for McDonald School, $r = 0.73$ for Kelly High School, and $r = 0.84$ for Campton School. All are significant at the 99% confidence level.

The 1976 summer samples were influenced by a period of decreased taconite processing. Despite the importance of independent meteorological and fugitive dust-emission factors and the assumption that the amount of amphibole material emitted is proportional to the amount of iron production, there appears to be some association between amphibole concentrations and the percent of normal iron production taking place during each week of sampling.

Correlation coefficients ($n = 10$) for the two sets of data (EPA and MDH samples, respectively) are: 0.64 and 0.78 for McDonald School; 072 and 0.79 for Kelly High School; 0.49 and 0.34 for Campton School. Only the samples

collected at Campton School do not correlate with percent iron production at the 95% confidence level.

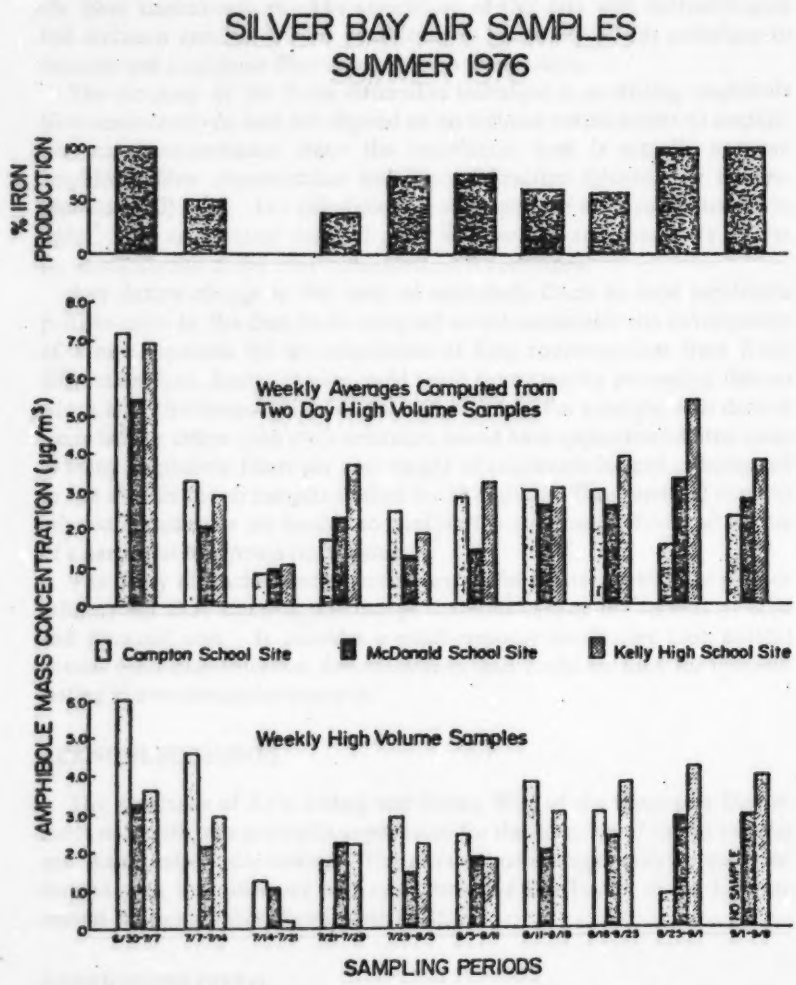

Figure 5. Amphibole mass concentrations determined for two independent sets of air samples collected at the same sites during the summer of 1976.

CONCLUSIONS

The X-ray diffraction analysis for amphibole mass concentrations in ambient air samples provides useful and detailed information about amphibole fiber concentrations. The association of the data with meteorological and emission conditions adds confidence to the ability of this technique to describe real amphibole fiber concentration fluctuations.

The accuracy of the X-ray diffraction technique in predicting amphibole fiber concentrations does not depend on an accurate measurement of amphibole mass concentration since the correlation used is actually between amphibole fiber concentration and X-ray diffraction intensity for the amphibole (110) peak. The calculation of an amphibole mass concentration in $\mu g/m^3$ with an external standard curve is, therefore, an unnecessary step as far as calculation of the fiber concentration is concerned.

Any future change in the ratio of amphibole fibers to total amphibole particle mass in the dust to be analyzed would necessitate the development of a new equation for the calculation of fiber concentrations from X-ray diffraction data. Such a change could result from taconite processing changes which alter the characteristics of the dust emitted. For example, dust derived from tailings rather than stack emissions would have approximately ten times as many amphibole fibers per unit weight of amphibole mineral as compared to the dust in the air samples studied for 1974-1976. Thus, periodic electron microscope analyses are needed to confirm the continued efficacy of the use of a particular fiber/mass relationship.

The X-ray diffraction technique is most useful for its capability to provide information that electron microscope methods cannot for reasons of time and financial cost. It provides a quick-response monitoring tool, enables annual mean-concentration determinations, and could be used for frequent testing in dust-abatement research.

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